

**MECHANICAL PROPERTIES AND
BIODEGRADABILITY OF CARBOXYLATED
NITRILE BUTADIENE RUBBER REINFORCED
WITH CELLULOSE NANOCRYSTALS**

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CELLULOSE NANOCRYSTALS**

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled “Mechanical Properties and Biodegradability of Carboxylated Nitrile Butadiene Rubber Reinforced with Cellulose Nanocrystals”. I also declare that it has not been previously submitted for the award of any degree and diploma or other similar titles of this for any other examining body or University.

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LIST OF SYMBOLS

°C	Degree Celsius
cP	Centipoise
g	Gram
M	Mole
min	Minute
µm	Micrometer
ml	Millilitre
mm	Millimeter
MPa	Megapascal
mV	Millivolt
nm	Nanometer
phr	Parts per Hundred Rubber
rpm	Revolutions per minute
T_g	Glass Transition Temperature
Wt. %	Weight Percentage
θ	Theta

LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
CMF, MFC	Cellulose Microfibers
CN	Acrylonitrile Group
CNCs, CNC	Cellulose Nanocrystals
CNF	Cellulose Nanofibers
CO ₂	Carbon Dioxide
Covid-19	Coronavirus Disease 2019
CrI	Crystallinity Index
DLS	Dynamic Light Scattering
DP	Degree of Polymerization
DSC	Differential Scanning Calorimetry
Eb	Elongation at Break
FTIR	Fourier Transform Infrared
H ₂ O ₂	Hydrogen Peroxide
H ₂ SO ₄	Sulfuric acid
HBr	Hydrogen Bromide
ISO	International Standard Organizations
KOH	Potassium Hydroxide
MCC	Microcrystalline Cellulose
NaClO	Sodium Hypochlorite
NaOH	Sodium Hydroxide
NBR	Nitrile Butadiene Rubber
NR	Natural Rubber
OH	Hydroxyl Group
OM	Optical Microscope
pH	Potential of Hydrogen
PPE	Personal Protective Equipment
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope
TEMPO	(2,2,6,6-tetramethylpiperidin-1-yl)oxy
TGA	Thermogravimetric Analysis

TSC	Total Solid Content
USD	United States Dollar
USM	Universiti Sains Malaysia
XNBR	Carboxylated Nitrile Butadiene Rubber
XRD	X-ray Diffraction
ZDEC	Zinc Diethyl Dithiocarbamate
ZnO	Zinc Oxide

**SIFAT MEKANIKAL DAN BIODEGRADASI GETAH NITRIL
BUTADIENA BERKARBOKSILASI DIPERKUATKAN DENGAN
NANOKRISTAL SELULOSA**

ABSTRAK

Penyelidikan ini bertujuan untuk mengukuhkan getah nitril butadiena berkarboksilasi (XNBR) dengan pengisi bio untuk menggalakkan biodegradasi tanpa menjejaskan sifat mekanikal XNBR filem. Oleh itu, kami membuat hipotesis bahawa nanokristal selulosa kristaliniti tinggi (CNC) dipilih sebagai pengisi bio untuk diadun dengan XNBR lateks. CNC telah diasingkan daripada serabut kapas melalui proses hidrolisis asid sulfurik. Isolasi CNC telah diadun dengan XNBR lateks sebagai bio pengisi untuk menghasilkan bio-nanokomposit filem melalui kaedah pengacuan filem. Kepekatan asid dan suhu hidrolisis adalah faktor yang mempengaruhi sifat CNC. CNC yang diekstrak telah dinilai dari segi sifat terma, saiz zarah, kestabilan dispersi, kehabluran, dan morfologi permukaan. Indeks kehabluran menurun kepada 62.57% untuk CNC yang diperolehi dengan 55% H₂SO₄ pada suhu 25°C (CNC 3). Suhu degradasi terma suspensi CNC adalah ~100°C dan 350°C. Saiz zarah CNC adalah antara 175-260 nm dengan potensi zeta (cas permukaan) antara -24.4 hingga -51.6 mV. Adunan CNC (CNC 1) dengan indeks kehabluran tertinggi dan kestabilan suspensi (72.23% dan -51.6 mV) ke dalam lateks XNBR membawa kepada peningkatan sifat mekanikal dan biodegradasi sehingga 5 wt% peningkatan beban. Kami menjangkakan hasil kajian ini sebagai langkah pertama pendekatan mampan antara hubungan struktur-sifat; mekanikal dan biodegradasi XNBR filem yang mengandungi pengisi CNC.

**MECHANICAL PROPERTIES AND BIODEGRADABILITY OF
CARBOXYLATED NITRILE BUTADIENE RUBBER REINFORCED WITH
CELLULOSE NANOCRYSTALS**

ABSTRACT

This research aims to reinforce carboxylated nitrile butadiene rubber (XNBR) with bio-filler to promote biodegradability without sacrificing the mechanical properties of XNBR film. Therefore, we hypothesized that the high crystallinity cellulose nanocrystals (CNCs) are the preferred bio-filler to be blended with XNBR film. The CNCs were isolated from cotton linter through a sulfuric acid hydrolysis approach. The isolated CNCs were incorporated with XNBR latex as a reinforcement filler to prepare XNBR/CNCs bio-nanocomposites films through film casting. The acid concentration and hydrolysis temperature were the controlling factors in obtaining CNCs. The obtained CNCs were evaluated in terms of thermal properties, particle size, dispersion stability, crystallinity, and surface morphology. The crystallinity index decreased to 62.57% for the CNCs obtained with 55% H₂SO₄ at 25°C (CNC 3). Thermal degradation temperatures of the CNCs suspensions were ~100°C and 350°C. The CNCs were found to have a particle size between 175-260 nm with zeta potential (surface charge) ranging from -24.4 to -51.6 mV. Incorporating CNCs (CNC 1) with the highest crystallinity index and suspension stability (72.23% and -51.6 mV) into XNBR latex led to the enhancement in mechanical properties and biodegradability with increased loading up to 5 wt%. We anticipate our results provide the first steps toward the sustainable approach of structure-property relationships towards mechanical and biodegradability of XNBR films that contain CNC fillers.

CHAPTER 1

INTRODUCTION

1.1 Research Background

For over two years after the outbreak of the Covid-19 pandemic, gloves have become one of the critical equipment in fighting against this Covid-19 virus. Healthcare workers and the community use personal protective equipment (PPE) like single-use disposable latex gloves and masks during the pandemic to protect them against the pathogen. The widespread use of PPE has induced a great concern regarding the waste disposal system. The quantities of PPE wastes generated worldwide since the Covid-19 outbreak is estimated at 1.6 million tonnes per day. The irresponsible disposal of these biomedical wastes from any sources has been referred to as potential sources of infectious pollutants. The mismanaged PPE wastes are believed to end up in open landfills or unregulated dumpsites, resulting in environmental impacts (Nsikak, 2021). One of the solutions to tackle the problem of these PPE wastes (latex gloves) is by introducing organic filler as one of its ingredients to be potentially biodegradable without sacrificing its mechanical properties. Dating back a few years, organic fillers; microcrystalline cellulose (MCC), cellulose microfibrils (CMF), cellulose nanofibrils (CNF), and cellulose nanocrystals (CNC) have caught the attention and motivated researchers to turn them into valuable sustainability products.

Many organic polymers or bio-renewable polymers can be utilized to obtain these micro or nanosize fillers. In this research, cotton linter is the sustainable source for isolating cellulose nanocrystals. The isolation of nanocrystals from cellulosic plants can be done through chemical, enzymatic and mechanical processes. In the way of obtaining isolated cellulose nanocrystals or cellulose nanowhiskers, strong acid

hydrolysis is used. According to Brinchi et al. (2013), the extraction of CNC from the cellulose source involved two stages: pre-treating the cellulose material to completely or partially eliminate hemicellulose and lignin. Controlled acid hydrolysis, which occurs in the second stage, eliminates the amorphous domains of the cellulose polymer and leaves the crystalline part of the polymer. Pre-treatment depolymerizes and solubilizes the lignin and hemicelluloses and involves pulping and bleaching processes. For pulping and bleaching, sodium hydroxide and hydrogen peroxide are used in this project, respectively.

The primary purpose and motivation of this study are to convert cheap and abundantly available cotton linter into cellulose, particularly cellulose nanocrystals that have good properties in terms of crystallinity, particle size, stability, etc. A few studies (Cao *et al.*, 2013; Taib *et al.*, 2020) have been reported using cotton linter as the cellulose source to isolate the cellulose nanocrystals. These studies mainly used a single controlling variable which deviates as compared to this study which used two controlling variables. Besides, the procedures employed in this study were more simplified. Therefore, this study will provide information on the characteristics of cotton linter-derived cellulose nanocrystals by using a new and simplified approach.

The cellulose nanocrystals obtained have been used to produce bio-nanocomposite films. The selected characterized cellulose nanocrystals were incorporated with carboxylated nitrile butadiene rubber (XNBR) latex to form XNBR/CNC bio-nanocomposite films. The carboxyl and acrylonitrile functional groups on the XNBR latex are expected to interact with the hydrophilic surfaces of CNC and improve the mechanical properties of the XNBR/CNC films. The films are fabricated to study their mechanical properties and biodegradability.

Numerous industries use cellulose nanocomposites, including packaging, optoelectronic, barrier, electrical, medicine, paper, and textiles (Feldman, 2015). The nanocellulose reinforced rubber nanocomposites are expected to become more popular and significantly advance in the future due to the advantages such as biodegradability, biocompatibility, renewability, improved mechanical properties and environmental friendliness (Zhou *et al.*, 2015).

1.2 Problem Statement

Owing to the vast application and availability of rubber latex, it has gained much attention from researchers. As for now, the Covid-19 pandemic is still happening worldwide; XNBR latex gloves are still in demand in many sectors. The increasing amount of non-biodegradable rubber wastes may cause specific environmental impacts. So, the effort of introducing bio-fillers or organic nanofillers in rubber has become an alternative and sustainable method to reduce rubber waste around the world. The extraction of cellulose nanocrystals from renewable sources of organic polymers and the development of bio-nanocomposites has become a significant research interest, especially in rubber product manufacturing. Therefore, isolation of cellulose nanocrystals from cotton linter has been proposed to widen the utilization of cotton linter.

In this study, an approach that has been used to isolate the cellulose nanocrystals (CNCs) from cotton linter is via sulfuric acid hydrolysis. In this approach, sodium hydroxide is used as one of the alkali treatment (pulping) agents to remove the lignin, whereas hydrogen peroxide is used as the bleaching agent. Besides, using sulfuric acid for hydrolysis, the cellulose nanocrystals obtained are believed to have a low yield, low thermal stability, and good suspension stability. A few parameters such

as hydrolysis temperature and acid concentration act as variables in this study. The cellulose nanocrystals obtained will be comparable for their properties in terms of particle size, suspension stability, thermal stability, and crystallinity.

The particle size and crystallinity of the CNCs may contribute different strength properties to the XNBR latex films. Therefore, in this research, a substantial study on the development of high crystallinity cellulose nanocrystals is essential to developing XNBR latex films with good mechanical properties and biodegradability.

1.3 Objectives

This research aims to develop carboxylated nitrile butadiene rubber (XNBR) latex films that are incorporated or reinforced with cellulose nanocrystals, which also have good mechanical properties and biodegradability. The specific research objectives are as follows:

- I. To characterize the cellulose nanocrystals from cotton linter.
- II. To obtain high crystallinity of cellulose nanocrystals to be incorporated with XNBR.
- III. To evaluate the mechanical and biodegradability properties of XNBR bio-nano composite films.

1.4 Scope of Research

In this research work, few studies were conducted to investigate the effect of the incorporation of CNCs in the XNBR latex films. In the first stage, the procedures and parameters used for cellulose nanocrystals isolation or extraction are investigated and analyzed through Dynamic Light Scattering (DLS), X-Ray Diffraction (XRD), Transmission Electron Microscope (TEM), Optical Microscope, Thermogravimetric

Analysis (TGA) and Fourier-transform infrared spectroscopy (FTIR) in order to obtain the good properties of nanocellulose fillers.

Besides, the XNBR latex films, which act as control samples, and CNCs-based XNBR latex films are investigated to determine the effect of incorporating the CNCs into the XNBR latex films. The mechanical properties of the XNBR latex films are evaluated by using ASTM D412 tensile test, and the tensile fracture is investigated using Scanning Electron Microscopy (SEM). A soil burial test is carried out to determine the biodegradability of the CNCs reinforced XNBR latex films.

1.5 Thesis Outline

This thesis consists of five main chapters:

Chapter 1: Briefly discuss the overview of the research, problem statement, objectives, and scope of the research work.

Chapter 2: Review the available literature and previous research findings related to the research interest.

Chapter 3: Show the research study's overall procedure, including information on the material specification, the equipment, and testing used, and the overall methodology flow of the study.

Chapter 4: Discusses the research's overall findings, including cellulose nanocrystals (CNCs) properties, mechanical properties, and biodegradability of the CNCs-based XNBR latex film.

Chapter 5: Summarizes and concludes the overall project and recommendations for future works.

CHAPTER 2

LITERATURE REVIEW

2.1 Synthetic Latex

Synthetic latex is an aqueous polymer dispersion that is produced by emulsion polymerization. Synthetic latex varies from natural rubber (NR) latex in how they are synthesized or collected and some differentiable features. Synthetic latex can be easily distinguished from NR latex in terms of a few characteristics such as particle size, shape, and size distribution. Synthetic latex has particles mostly spherical with a simpler form of structure, while particles of NR latex have complex geometrical shape and structure. Besides, the particle size and particle size distribution of synthetic latex are smaller and narrower as compared to NR latex. The typical number-average particle diameter of synthetic latex and NR latex is 50 – 100 nm and 5 μm respectively (Blackley, 1997).

Synthetic latex has lower wet-gel strength in contrast to NR latex which is a disadvantage to synthetic latex and this is due to several principal factors; small particles size, the high molecular mass of polymer molecules, molecular complexity of the polymer molecules, and high ratio of hydrophilic colloid stabilizer to the polymer during compounding or application. The high molecular mass of polymer and molecular complexity are attributed to the polymer synthesis method of free-radical addition polymerization, which leads to the formation of highly-branched polymer and crosslinks to form high gel content polymer. The resulting synthetic latex films tend to absorb water easily and the latex deposits dried slower than NR latex. Synthetic latex is known to lack proteinaceous substances and other natural products, therefore, coagulation, putrefaction and odours are not normally observed or developed (Blackley, 1997).

2.1.1 Acrylonitrile Butadiene Rubber (NBR)

Acrylonitrile butadiene rubber latex or nitrile latex is produced by emulsion polymerization of acrylonitrile and butadiene. It is the copolymers of diene and vinyl-unsaturated nitrile. NBR latex has good properties such as high oil resistance, heat resistance and good compatibility with several compounding ingredients. NBR latex, which is produced through emulsion polymerization, can achieve acrylonitrile content between 15 to 50%. The increment in the acrylonitrile content in the NBR latex increases the polarity and solubility parameters of the copolymer. Besides, it also improves the resistance against chemicals such as oils and glass transition temperature (T_g) of the NBR, from -60 to -10 °C (Martínez, 2002). Figure 2.1 shows the chemical structure of NBR latex.

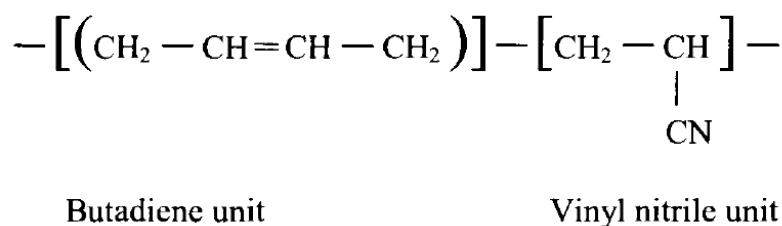


Figure 2.1: Chemical structure of NBR (Martinez, 2002).

One of the characteristics of NBR latex is that it is typically free from NR proteins which may cause allergic reactions in some people. NBR latex containing around 18 to 25% acrylonitrile content is referred to as ‘low acrylonitrile’ latex; 26 to 40% is ‘medium acrylonitrile’ and above 40% is called ‘high acrylonitrile’ (Hill, 2018).

As of 2020, the NBR latex market size was valued at over USD 3.5 billion and is expected to increase further in the next seven years. The growing demand for gloves, especially medical gloves in the healthcare industry, contributes most to the market (Global Market Insight, 2021). Figure 2.2 below shows the estimated NBR latex market share of two different types of gloves from 2020 to 2027.

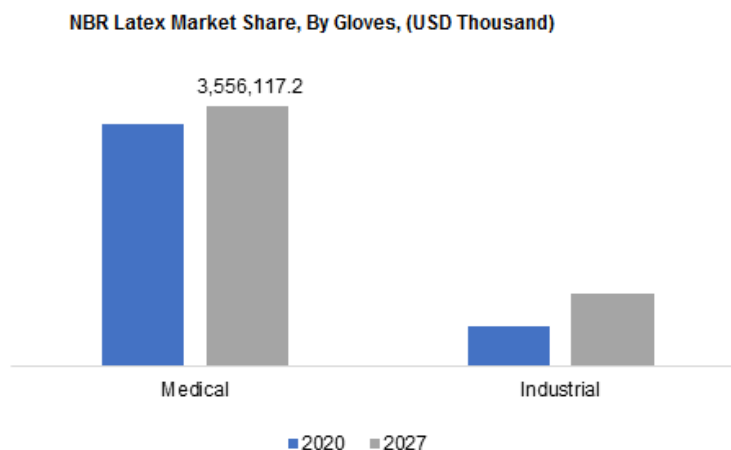


Figure 2.2: Estimated NBR latex market share of medical and industrial gloves (2020-2027) (Global Market Insight, 2021).

2.1.2 Carboxylated Nitrile Butadiene Rubber (XNBR)

Carboxylated NBR is also known as XNBR and is an improved version of NBR. XNBR latex is one of the main latices that produce synthetic gloves worldwide. XNBR latex is produced through an emulsion polymerization method where acrylonitrile and 1, 3 butadiene are polymerized in an aqueous emulsion with an emulsifier (Daud *et al.*, 2018). In XNBR latex, a carboxyl group is introduced into the polymer backbone to saturate the butadiene segment. For instance, a small amount of methacrylic acid (MAA) can be incorporated into the formulation to add this carboxyl group. The resulting ionic groups in the polymer backbone allow crosslinking of the polymer through ionic mechanisms using Zinc oxide (ZnO) or alkali, such as potassium hydroxide (KOH). The butadiene segment also allows crosslinking through the reaction with sulfur (Hill, 2018).

With the C=C double bonds of the butadiene segment in the XNBR, there are covalent crosslinking sites that make thermal curing with either peroxides or sulfur and accelerators. Besides, the carboxylic group in XNBR provides crosslink sites for forming ionic and covalent bonds or linkages (Lenko *et al.*, 2013). Zinc Oxide (ZnO) is

an effective ionic crosslinking agent to yield XNBR vulcanizates with high tensile strength. Figure 2.3 below shows the reaction between a carboxylic group in XNBR and ZnO.

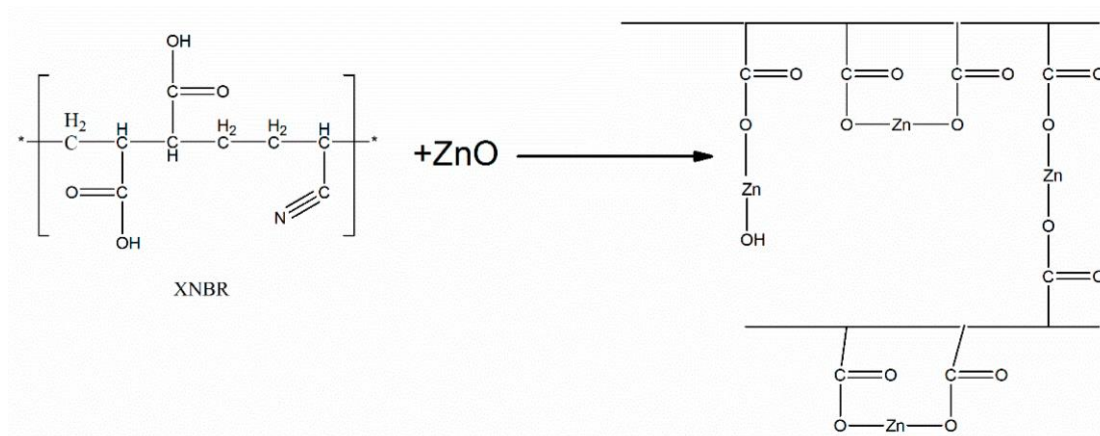


Figure 2.3: Reaction between a carboxylic group in XNBR and ZnO (Paran et al., 2020).

The in-situ interfacial reaction such as grafting, addition, crosslinking, or esterification between an unsaturated carboxylic group in the rubber with metallic oxide form the salt-bondings, which increase the mechanical properties of rubber blends (Jiahui *et al.*, 2021).

The ionic crosslinking leads to higher tensile strength than sulfur crosslinking in XNBR latex or elastomer. In the XNBR latex, there are ionic and sulfur crosslinking, giving them a higher tensile strength and modulus than NR latex. Due to the high modulus, stresses might build up in the latex films upon drying and tend to shrink (Hill, 2018).

2.1.3 Latex Compounding and Ingredients

Compounding involves the modification of a rubber or elastomer or a polymer blend and other compounding materials to optimize the properties to meet specific performance parameters and service applications. The ingredients formulation is determined according to the product performance requirements (Rodgers and Waddell, 2013). Unlike solid rubber, the compounding system of latex must be in a liquid phase rather than a dry phase. Thus, powder from water-insoluble compounding ingredients is converted to stable aqueous suspensions by grinding in a pebble mill with stabilizers and dispersing agents. The water-insoluble liquids, such as accelerators, etc., are converted into a water-oil emulsion using the colloid mill. The compounding ingredients like a vulcanizing agent, accelerator, activator, and antioxidant are fundamental to latex compounding (Button, 1957).

A good quality compounded latex has several characteristics; consistent properties and conformation to the compounded latex specification. The following phases of latex compounding can be outlined: preparation of the raw material, including the compounding materials, maturation, final compounding, and testing. In latex compounding, the predetermined compounding procedure should be followed, and latex and other compounding ingredients should be weighed accurately to prevent possible variability in the properties of the latex-dipped products. Before adding compounding components, the latex is transferred into the compounding tank in a way that prevents coagulum formation or air bubbles. The latex needs to be continuously stirred during the compounding process for the compounding ingredients to be dispersed in or homogeneously mixed with latex. The latex compound is then left for maturation and later taken for dipping or stored in a container below or around room temperature (Hill, 2018).

The compounding ingredients used in rubber latex are divided into curing agents, accelerators, fillers, stabilizers, antioxidants, pigments, thickening and wetting agents and other ingredients such as viscosity modifiers, etc. (Joseph, 2013).

Sulfur is the widely used crosslinking agent for natural and synthetic rubber-like acrylonitrile-butadiene rubber. Three types of crosslinks are formed during sulfur vulcanization; monosulphidic, disulphidic and polysulphidic. Polysulphidic linkage is prone to be formed when a high amount of sulfur is used for compounding. The sulfur used for latex compounding should be easily dispersed in water and colloidal sulfur is one of the preferable options (Joseph, 2013).

Accelerators are organic chemicals that facilitate the vulcanization process by shortening the vulcanization time. It also enables latex to obtain optimum physical properties with reduced quantities of sulfur (Button, 1957). There are primary and secondary accelerators used in latex compounds. Dithiocarbamates are the class of primary accelerators, while thiazoles and thiurams are secondary accelerators used along with dithiocarbamates (Joseph, 2013).

In terms of activators, zinc oxide can enhance or facilitate the action of accelerators (Joseph, 2013). However, the colloid stability of the ammonia-preserved NR latex compounds may decrease due to the presence of zinc oxide and phenomena of zinc-oxide thickening and possibly gelation (Blackley, 1997ii).

Antioxidants are chemicals that are used to retard the deterioration and oxidation of rubber products. They consist of waxes, amines, phenolics and amine condensation products (Button, 1957). The amine-type antioxidants will induce discoloration upon ageing due to resinous in nature resulting in difficulty in dispersing in the rubber latex. Besides, phenolic antioxidants are most commonly used in latex and these water insoluble liquid antioxidants are added into latex as water-emulsion (Joseph, 2013).

Table 2.1 shows the types and the function of the latex compounding ingredients (Suhaimi, 2016).

Table 2.1: Type and function of the latex compounding ingredients (Suhaimi, 2016).

Typical Ingredients and Function	Description
pH modifier: Potassium Hydroxide (KOH)	Maintaining the colloidal stability of latex compound
Stabilizer: Potassium Oleate	Promote latex stability, viscous modifier
Activator: Zinc Oxide	Regenerate and activate accelerators for vulcanization to happen
Accelerator: ZDEC	Control and facilitate the rate of crosslinking process
Antioxidant	To provide protection against degradation during exposure
Curing agent: Sulfur	Promote crosslinks formation between rubber molecules in latex

2.1.4 Preparation of Latex Compounding Ingredients

In compounding, the ingredients of the water-soluble solids or liquids are added into latex as aqueous solution while water-insoluble solids are dispersed, and water-insoluble liquids are emulsions. The compounding ingredients, whether in aqueous solutions, dispersions or emulsions, should have a particle size, colloid stability, and pH that are similar or corresponding to the latex for them to be mixed homogeneously with latex (Blackley, 1997).

In preparing aqueous dispersions of solid ingredients, it's first by preparing a coarse slurry of the powdered ingredient with water containing small amounts of dispersing agent and colloid stabilizer. To obtain a dispersion with a small particle size, the slurry is subjected to grinding in a mill for some time. Figure 2.4 shows the schematic illustration of the principle of the ball mill (Blackley, 1997).

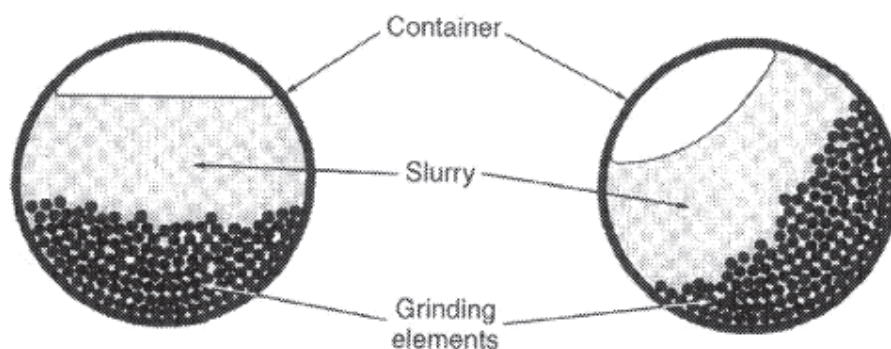


Figure 2.4: Schematic illustration of the principle of the ball mill (Blackley, 1997).

The mills that can disintegrate any particle aggregates and achieve a smaller particle size of dispersions through high shear action are, for example, ball mills, pebble mills, sand mills, vibration mills, attrition mills, and ultrasonic mills. These mills are suitable for preparing aqueous dispersions of powdered ingredients such as zinc oxide, kaolinite clay, etc. Besides the grinding, as mentioned earlier, colloid mills that do not

significantly affect the particle size of dispersions are suitable for preparing ingredients such as sulfur, accelerator and antioxidants (Blackley, 1997). The rotary ball, bead, and pebble mills are commonly comprised of a cylindrical container and is rotated about its cylindrical axis in a horizontal plane. The slurry component is added to the mills along with some balls, beads, or pebbles. The motion of the balls moving against each other and wall of the container as a combination of friction, attrition and impact result in the reduction of particle size of an aqueous dispersion.

In preparing oil-in-water emulsions of compounding ingredients to be added to latex, it is first by making a coarse suspension of oil droplets in water in the presence of an emulsifying agent and then subjected to a refining process. The coarse suspension is initially made by adding oil to water under agitation for the emulsions to be formed easily. Phase-inversion method in which increasing quantities of aqueous phase are added to the oil phase under agitation can also be applied. With this method, as a more aqueous phase is introduced to the emulsion, water-in-oil emulsion forms first followed by oil-in-water emulsion (Blackley, 1997).

The two most popular techniques for making coarse emulsions are the direct and soap-in-situ methods. The direct method involves dissolving the emulsifying agent, colloid stabilizer, thickener, etc in the water followed by oil addition under high-speed stirring. Carboxylate soap is used to aid the dispersion in the soap-in-situ method. While the alkali component of the soap is dissolved in water with colloid stabilizer and thickeners, the fatty-acid component is dissolved in oil. The oil and aqueous phases are then mixed while vigorously stirring, allowing emulsification to happen naturally. (Blackley, 1997).

2.1.5 Latex Dipping for Gloves

Latex gloves are commonly manufactured by batch dipping or continuous dipping processes. Batch dipping is used to manufacture irregular shaped articles in small volumes. Continuous dipping is the most commonly used dipping method in the industry nowadays due to its high-speed continuous dipping lines with high output (Joseph, 2013). Latex dipping processes include straight dipping, coagulant dipping and heat-sensitized dipping. Coagulant dipping involves the application of coacervate to facilitate the formation of latex deposits compared to straight dipping. The latex compound used for heat-sensitized dipping is typically heat sensitive and former need to be heated during dipping (Blackley, 1997). The typical flow chart of the latex glove manufacturing process is shown in Figure 2.5 (Akabane, 2016).

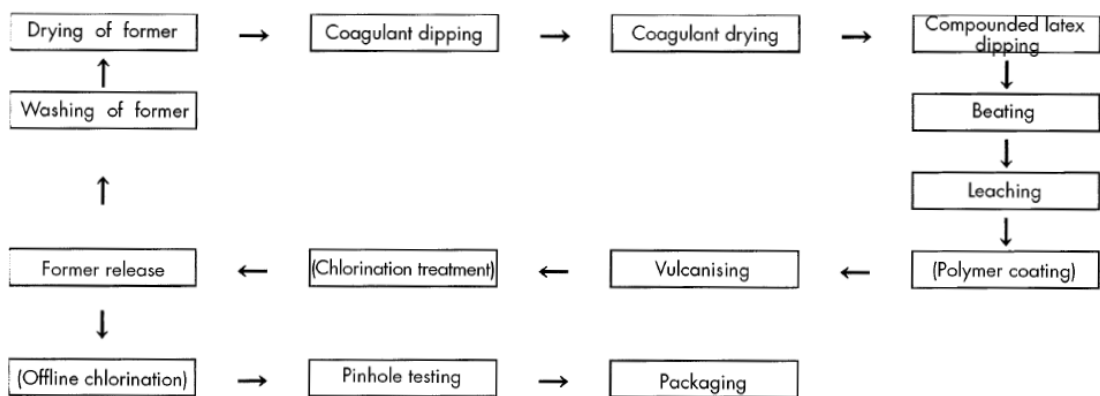


Figure 2.5: Flow chart of latex glove manufacturing process (Akabane, 2016).

Most rubber gloves are produced by coagulant dipping. The latex is destabilized by coagulant during latex dipping. Coagulant dipping can be divided into anode process and Teague process. Anode process describes that coagulant is to be first deposited on the former surface before dipping in latex. The coagulants suitable for dipping are calcium salts; calcium nitrate and calcium chloride. On the other hand, the Teague process is opposite to the anode process in which the former is dipped with latex first then only dipped with coagulant (Akabane, 2016).

In latex dipping, dwell time depends upon the thickness of the films going to be produced; the longer the dwell time, the greater the film thickness. Latex drying can be done by direct gas heating, radiant heating or hot air in an oven with formers rotating continuously to prevent any thickness variation (Hill, 2018). The formers are passed through a hot air oven in an automated production with a low initial temperature of 80°C to prevent a high initial drying rate (Blackley, 1997). Figure 2.6 shows the schematic diagram of the glove dipping process (Groves and Routh, 2017).

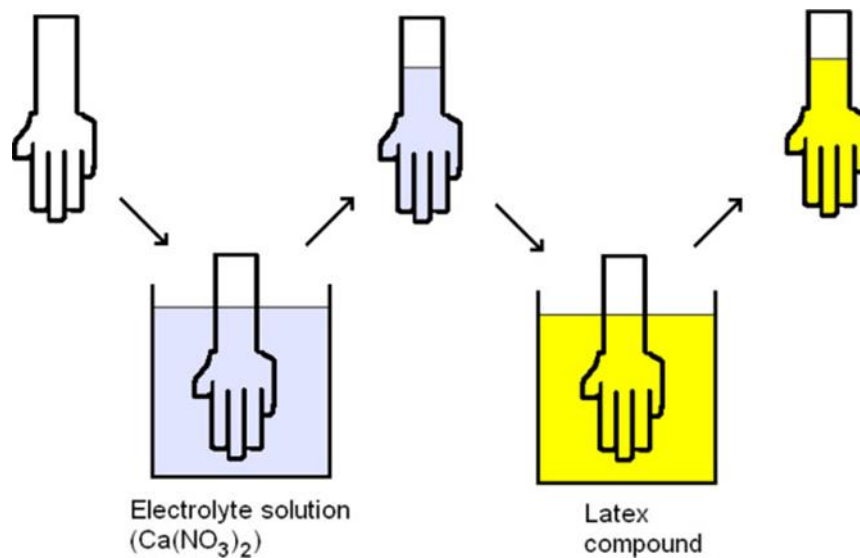


Figure 2.6: Schematic diagram of glove dipping process (Groves and Routh, 2017).

In leaching, there are wet-gel leaching and dry-gel leaching. Wet-gel leaching is more efficient than dry-gel leaching since water can penetrate the films and remove water-soluble substances; residual coagulant, water-soluble compounding additives present in films more easily. The leaching medium used is typically water at a temperature in the range of 60-80°C. The water should be replaced at specific intervals to remove leached substances (Hill, 2018; Blackley, 1997).

Vulcanization of latex films is usually done separately with latex drying, although it is convenient to be done together. Latex films are subjected to a heating medium of hot air at vulcanization temperature in the range of 100-150°C in an

automated production. There is so-called high humidity vulcanization with artificially controlled humidity, which permits the higher temperature to be used to induce crosslinking reaction without concerning the problem of film overdrying (Blackley, 1997; Hill, 2018).

Before stripping off the latex gloves from formers, surface treatment is applied to facilitate the stripping process and to prevent gloves from adhering to the former. Dusting gloves with talc, silica, and crosslinked starch is one of the treatments. Besides, chlorination treatment can be done on gloves by creating a thin layer of chlorinated rubber on the glove surface, thus preventing tackiness. On the other hand, gloves can be taken for polymer coating by dipping in a diluted acrylic or polyurethane aqueous dispersion (Akabane, 2016). Stripping of gloves can be carried out either manually or automatically. Automatic stripping is carried out using water jets, compressed air, rotating flaps or brushes, or any mechanical device (Hill, 2018).

2.2 Cellulose

Cellulose is the most abundant, biodegradable and recyclable polysaccharide in the world, composed of crystalline and amorphous regions (Younas *et al.*, 2018). Cellulose is sustainable natural polymeric material characterized by biodegradability, hydrophilicity, and wide-ranging chemical-modifying capacity (Nunes, 2017). The basic chemical structure of cellulose consists of a dimer called cellobiose which acts as a repeated segment. Figure 2.7 shows the chemical structure of cellulose (Habibi *et al.*, 2010).

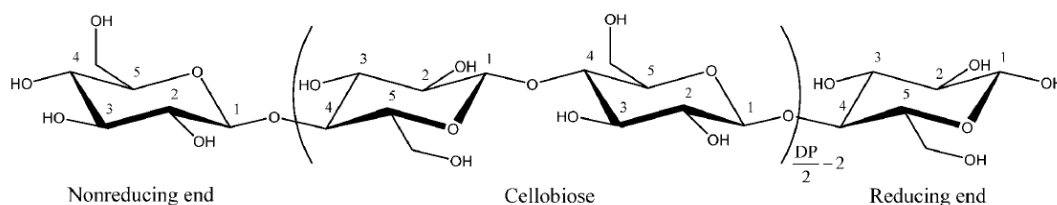


Figure 2.7: Chemical structure of cellulose (Habibi *et al.*, 2010).

The polysaccharide; cellulose with a chemical formula of $(C_6H_{10}O_5)_n$ consists of a linear chain with repeating units from hundreds to thousands. Cellulose can be found in various organic polymers; 90% in cotton fiber, 60% in hemp, 50% in wood and 40% in bamboo fibers. The abundant available hydroxyl groups on the cellulose can form hydrogen bonding with other groups on the same or neighboring chains. The cellulose has high strength and stiffness due to its linearity and extensive amount of hydrogen bonding formation (Song, 2017). Figure 2.8 shows the hydrogen bonding network in cellulose structure (Habibi *et al.*, 2010).

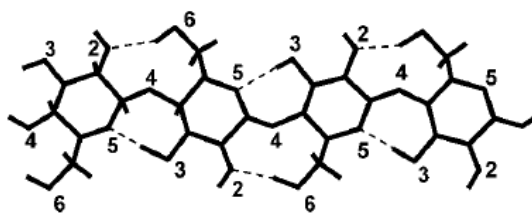


Figure 2.8: Intramolecular hydrogen bonding network in cellulose structure (Habibi *et al.*, 2010).

Other than woods, plant fibers (cotton, hemp, flax), marine animals (tunicate) or algae, invertebrates are origin sources of the cellulose (Rallini, 2017; Lavoine *et al.*, 2012). There are several cells in a single filament of all natural plant fibers and they are formed out of cellulose-based crystalline microfibrils which are attached to a layer by amorphous lignin and hemicellulose (Peponi *et al.*, 2014). Figure 2.9 illustrates the typical sources of cellulose and details of the cellulose microfibrils structure (Lavoine *et al.*, 2012).

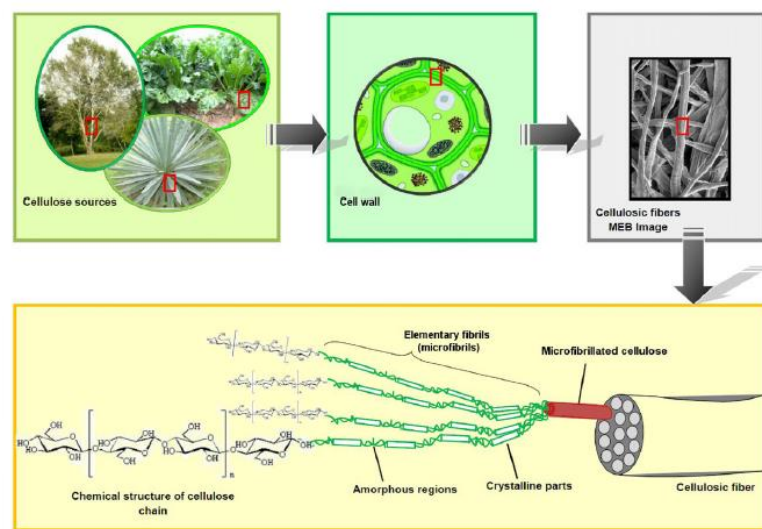


Figure 2.9: Cellulose sources and cellulose microfibrils structure (Lavoine *et al.*, 2012).

The degree of polymerization (DP) of cellulose is dependent on cellulose source, extraction method, and measurement techniques, e.g., cotton has $DP > 10,000$, and plant fiber has DP ranging from 800 to 10,000 (Younas *et al.*, 2018). Depending on the crystal structure or polymorphs of cellulose, it can be categorized into cellulose I, II, III, and IV. Cellulose I is found in nature and exists in two allomorphs, $I\alpha$ and $I\beta$. Cellulose II or regenerated cellulose, which appears to be the most stable crystalline form, arises after recrystallization with aqueous sodium hydroxide. Cellulose III can be obtained by ammonia treatment of cellulose I and II, and cellulose IV is the modification of cellulose III (Song, 2017; Lavoine *et al.*, 2012).

2.2.1 Nanocellulose

Nanocellulose designates materials composed of cellulose nanocrystals (CNC), cellulose nanofibrils (CNF), cellulose microcrystals, and cellulose microfibrils. Figure 2.10 below shows the transmission electron microscope (TEM) images of CNC and CNF and scanning electron microscope (SEM) images of bacterial cellulose (BC) (Abitbol et al., 2016).

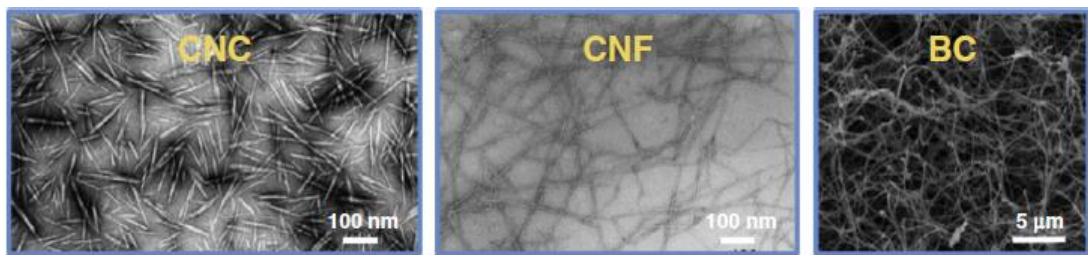


Figure 2.10: TEM images (CNC and CNF) and SEM image (BC) (Abitbol et al., 2016).

The microfibrils in cellulose are built from bundles of finer fibrils that are long, containing 2-30,000 cellulose molecules in cross section and diameter of 10-30 nm. The nanofibrils comprise a large part of ordered crystallites (60-80%) and a lesser part of amorphous domains (Peponi *et al.*, 2014).

Nanocellulose is renewable, lightweight, and inexpensive to produce. The two primary groups of nanocellulose which are used as filler in nanocomposites are cellulose nanocrystals (CNC) and nanofibrillated cellulose (NFC). Nanofibrils are generally obtained from natural fibers; microcrystalline cellulose (MCC) and microfibrillated cellulose (MFC) by using chemical or mechanical pathways (Feldman, 2015; Nunes, 2017).

Cellulose nanocrystals (CNC) possess potential in many applications due to their extraordinary properties such as biocompatibility, biodegradability, high crystallinity, high modulus, high mechanical strength, and high aspect ratio. However, the hydrophilic nature of CNC presents difficulty in its dispersion in a hydrophobic

polymer matrix or non-polar media. This is due to CNCs tend to form aggregates in the presence of polar groups (Younas *et al.*, 2018). The hydroxyl groups on CNCs enable easy incorporation into water-soluble polymers. The hydroxyl groups can be modified with other chemical groups to facilitate the CNC's dispersion in other polymeric matrices (Roman and Winter, 2004). Cellulose nanocrystals can be covalent and non-covalent surface modified. The modification can reduce the tendency of CNC aggregation through the reduction of hydrogen bonds, increasing the compatibility between filler and matrix. Cellulose nanocrystals are also called microcrystals, whiskers, nanoparticles, nanocrystals, nanofibers, or microcrystallites (Habibi *et al.*, 2010).

2.2.2 Isolation of Cellulose Nanocrystals

Cellulose nanocrystals (CNC) can be isolated from various sources such as cotton, wood, tunicates, ramie, softwood kraft pulp and recycled pulp. CNCs can be obtained from bulk of cellulose through chemical or mechanical treatments to separate out crystalline phase. The isolation techniques involve commonly used acid hydrolysis, (2,2,6,6-tetramethylpiperidin-1-yl)oxy (TEMPO) mediated oxidation, enzymatic hydrolysis, homogenization and mechanical disintegration (Younas *et al.*, 2018). The main method used to isolate CNC from any cellulose sources or cellulosic fibers is acid hydrolysis. Through this method, glycoside bonds in the amorphous region of cellulose are broken and left with the crystallites. The CNCs obtained are rod-like particles with high degree of crystallinity, width dimensions of 3-10 nm and an aspect ratio between 5-50. In the preparation of CNC based on strong sulfuric acid hydrolysis, there are stringently controlled conditions of temperature, time, agitation, acid concentration and ratio of acid to cellulose (Peponi *et al.*, 2014).

Generally, concentrated mineral acids such as sulfuric or hydrochloric acid are used for the hydrolysis process. The hydrolysis is stopped by rapid dilution of the acid when the appropriate level of glucose-chain depolymerisation is reached. Centrifugation and extensive dialysis is then employed to remove the acid and followed by sonication to disperse the individual particles of cellulose in order to yield a stable aqueous suspension (Fleming *et al.*, 2001; Brinchi *et al.*, 2013). Figure 2.11 shows the CNC isolation process by acid hydrolysis (Fortunati *et al.*, 2013).

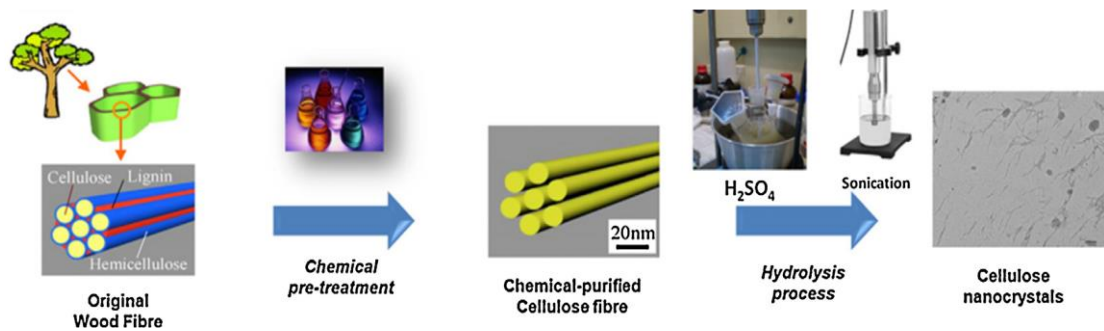


Figure 2.11: CNC isolation process (Fortunati *et al.*, 2013).

According to Habibi *et al.* (2010), in the CNCs isolation, other than sulfuric acid and hydrochloric acid, phosphoric and hydrobromic acids also can be used for hydrolysis. The dispersion of CNCs is limited and their aqueous suspensions tend to flocculate when it is prepared through hydrochloric acid hydrolysis. In the case of sulfuric acid is used, the acid reacts with the surface hydroxyl groups of cellulose by esterification process to produce charged surface sulfate esters which promote dispersion of the CNCs in water. The negatively charged CNC is induced by the sulphate groups attached to the cellulose, which also causes repulsion between the cellulose particles. The introduction of acidic sulphate groups to the surface of CNC jeopardises their thermal stability, though. The typical concentration value of the sulfuric acid used in hydrolysis reaction to obtain CNCs is 65% and the temperature ranges from room temperature up to 70°C. The hydrolysis time can be varied from 30 min to overnight depending on the temperature used.

According to the research work conducted by Cao *et al.* (2013), the fabrication of CNCs from cottonseed linter is done through acid hydrolysis with concentrated sulfuric acid (64%) under vigorous stirring at 60°C for 2 hours. The suspension is then washed with water by successive centrifugation and dialyzed against deionized water until neutral pH. A stable suspension of CNCs is then obtained after concentrating by vacuum rotation evaporation. The obtained CNCs are then used to reinforce nitrile rubber for the preparation of nanocomposite material. The nanocomposite is prepared by mixing the water suspension of CNCs and NBR latex directly.

The synthesis of CNCs from cotton linter microcrystalline cellulose is also carried out by Taib *et al.* (2020). The cotton linter is added to different concentrations of HCL acid. The solution is then hydrolysed at 100°C for 60 minutes with continuous stirring. The mixture is then quenched in an ice tube to stop the reaction. It is then rinsed with distilled water and centrifuged for 30 minutes at 3000 rpm. The supernatant is replaced by new distilled water and centrifuged again for five times. It is then dialysed and immersed in distilled water until neutral pH is achieved. The suspension is then freeze-dried and kept at room temperature. From this isolation method, the size of the CNC obtained is below 100 nm and the crystallinity index is around 60% at higher concentration of acid. It is also found that the highest thermal stability is pronounced at CNCs produced with lowest concentration of acid. The incorporation of CNCs into NBR composites proved to enhance the mechanical properties (tensile strength, modulus and elongation at break) but no significant effect on tear strength.

Atakhanov *et al.* (2019) isolated CNCs from cotton linter by first alkali treated the cotton linter in 1 M sodium hydroxyl solution and bleached with 4% hydrogen peroxide at 120°C for 2 hours. The cotton linter then washed with distilled water and dried at 100°C for 4 hours. Acid hydrolysis is then performed by slowly adding sulfuric

acid under continuous stirring to a cellulose/water suspension placed in an ice water bath until the predetermined acid concentration. The suspension is then heated at different temperatures for a certain duration with continuous stirring. The final suspensions are centrifuged, dialyzed in distilled water, microwave irradiation treated, ultrasonicated and homogenized.

The isolation of CNCs from rice straw cellulose by acid hydrolysis is done by Jiang and Hsieh (2013). The cellulose is added with preheated (45°C) sulfuric acid with concentration of 64% at acid-to-cellulose ratio of 8.75 ml/g. The hydrolysis is done at 45°C under constant stirring and is stopped by quenching with cold water and the suspension is centrifuged to collect the sediment which is then dialyzed against water. Further centrifugation is done to yield the supernatant. The CNC suspension is then ultrasonicated in an ice bath to disperse CNCs. The sulfuric acid hydrolysis is able to produce highly crystalline rod-like CNCs with similarly negative surface charges and sulfate contents. However, the yields and dimensions of CNCs decrease with longer hydrolysis time.

Wilson *et al.* (2013) used chemical-treated soy hulls to isolate CNCs through acid hydrolysis. The hydrolysis is performed at 40°C for 30 or 40 minutes under vigorous and constant stirring. The acid-to-cellulose ratio used is 30 ml/g. The suspension is diluted with cold water (10 fold) to stop the hydrolysis. It is then undergoing centrifugation twice to remove the excess acid. The precipitate is then dialyzed with tap water to remove non-reactive sulfate groups, salts and soluble sugars until neutral pH is reached. After that, the suspension is treated with a disperser and sonicated. The colloidal suspension is added with a few drops of chloroform to prevent bacterial growth before storing in a refrigerator at 4°C. The long hydrolysis time resulted in shorter length of nanocrystals and some damage to the crystalline structure